



The Use of Ester Co-Solvent Based Low Temperature Electrolytes in Experimental and Large Capacity Prototype Graphite-LiNiCoAlO₂ Lithium-Ion Cells

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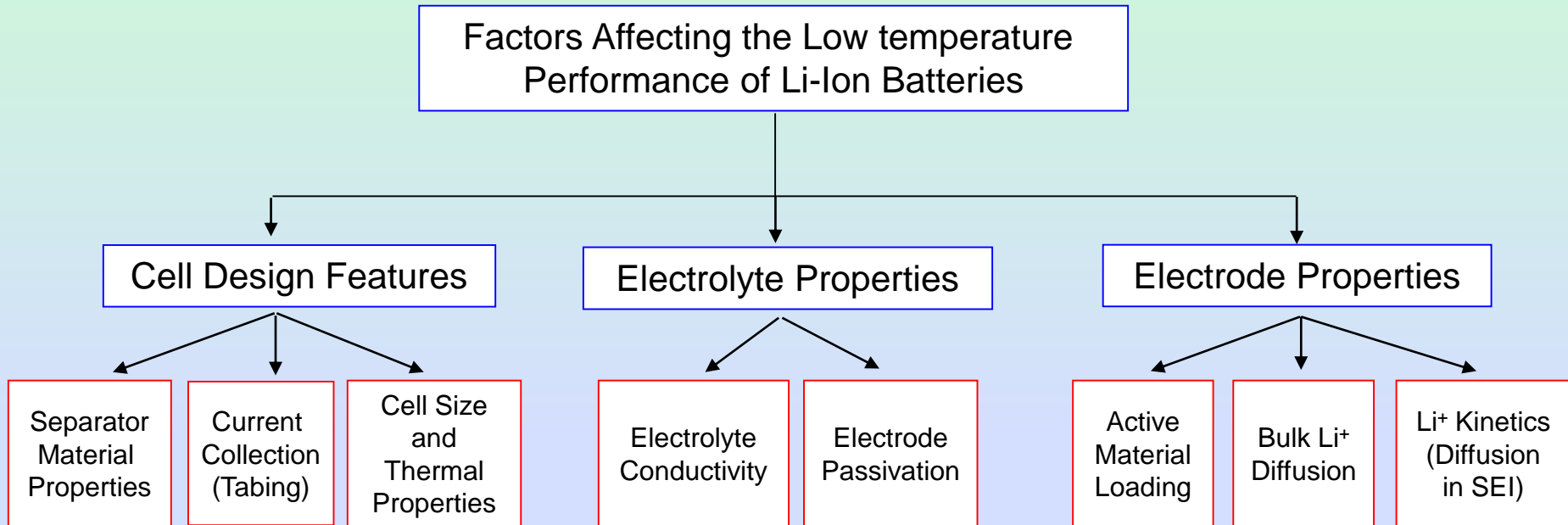
Outline

- ***Background***
- ***Objectives and Approach***
- ***Development and Demonstration of Heritage Carbonate-Based Electrolyte***
 - ***MSP'01 Mission, MER Mission, MSL Mission***
- ***Development and Demonstration of Ester-Containing Electrolytes***
 - ***InSight Mission***
- ***Development of Electrolytes for Future Ocean Worlds Missions***
 - ***Large format and small format (18650) cell approaches***
 - ***Yardney Large Capacity Prototype Cells***
 - ***Quallion Prototype BTE Cells***
 - ***E-One Moli 18650-size Cells***
- ***Conclusions***



Low Temperature Lithium Ion Electrolytes

Electrolyte Development: Approach/Background



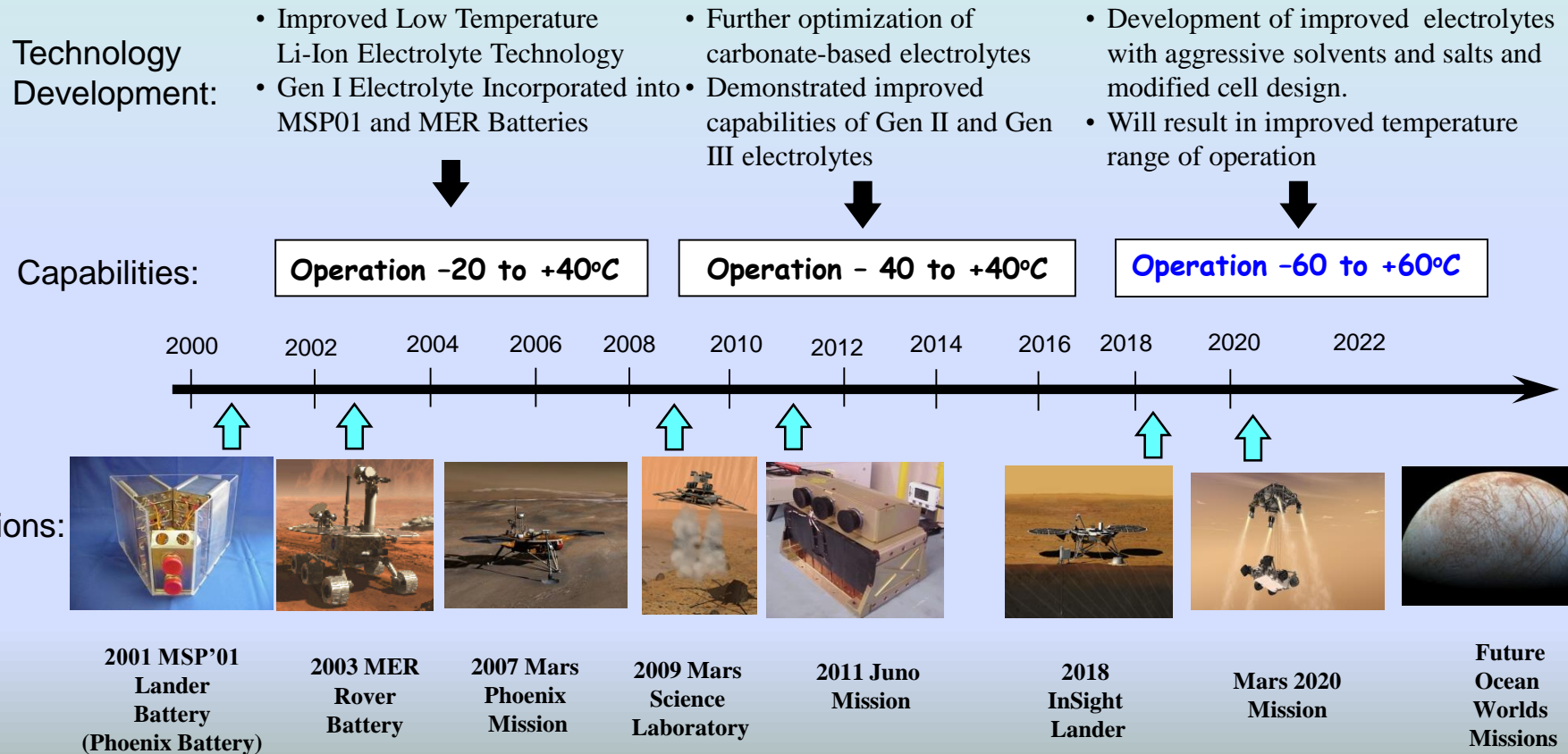
- Of these factors, the electrolyte properties have the most dramatic impact on low temperature performance (i.e., if the the electrolyte is frozen the cell/battery will not operate).
- Sufficient electrolyte conductivity at low temperature is not sufficient to ensure efficient operation due to potential reactivity leading to poor kinetics and/or inadequate life aspects.
- To enable very low temperature operation (< - 40°C), high diffusivity electrode materials must be identified coupled with improved cell design.



Development of Low Temperature Lithium Batteries

Vision and Goal

Goal: To develop rechargeable lithium-based cells for future NASA applications which are capable of operation over a large temperature range, especially at low temperatures (-60° to $+60^{\circ}\text{C}$).





2003 Mars Exploration Rover- Rover Batteries

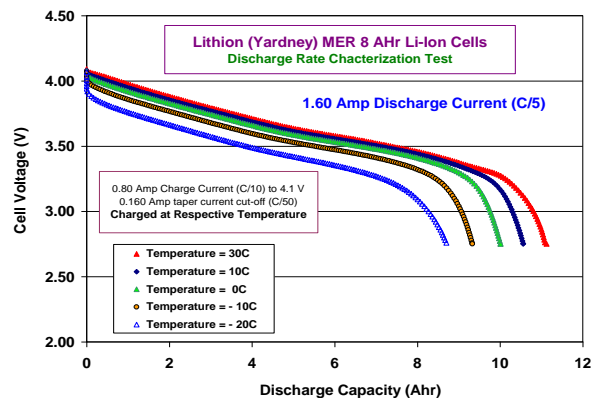


- Lithium-ion technology was used for '03 MER Rovers
- Heritage chemistry, including electrolyte, adopted from MSP'01
- Opportunity has been operational since landing on Mars on 1/25/2004

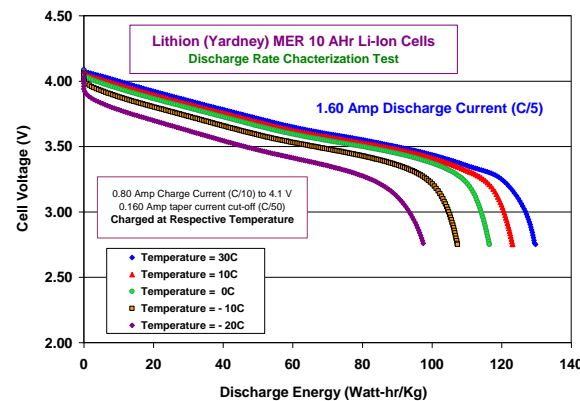
Rover Battery Requirements

- Voltage : 32-24 V
- Capacity: 16 Ah (BOL) at RT and 10 Ah at -20°C (BOL)
- Load : C/2 max at RT; Typical C/5
- Temperature : Charge at $0-25^{\circ}\text{C}$ and discharge $>-20^{\circ}\text{C}$
- Light weight and compact
- Long cycle life of over 300 cycles
- Long storage life of over 2 years

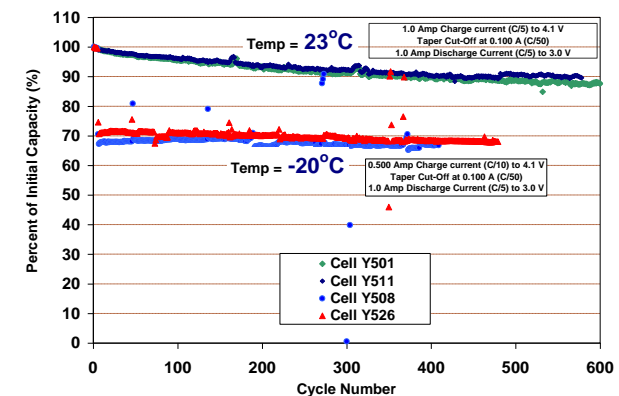
Discharge Capacity (Ah)



Discharge Energy (Wh/kg)



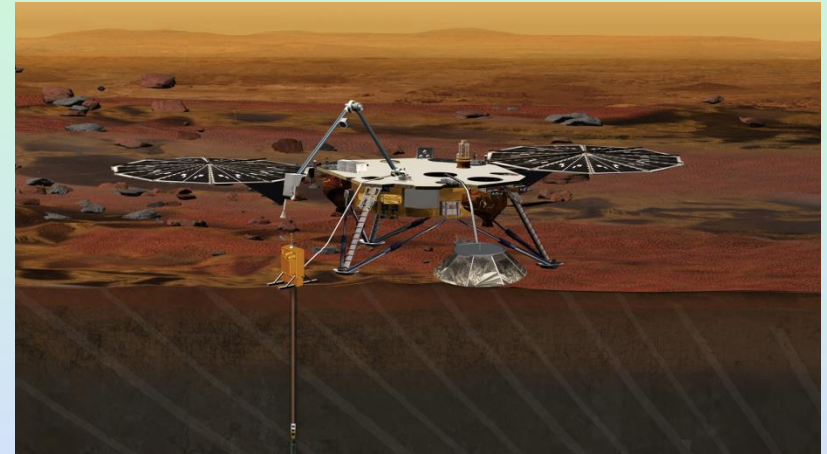
100% DOD Cycling Life



Cells contain 1.0M LiPF_6 EC+DMC+DEC (1:1:1) (Range of operation -20 to $+40^{\circ}\text{C}$)

NASA's Mars InSight Lander

- **Anticipated Launch Date: May 2018**
- InSight (Interior Exploration using Seismic Investigations, Geodesy and Heat Transport) is a NASA Discovery Program mission that will place a single geophysical lander on Mars to study its deep interior.
- Mission will consist of a spacecraft built by Lockheed Martin Space Systems Company based on a design that was successfully used for NASA's Phoenix Mars lander mission
- **Science Goals:**
 - InSight is a terrestrial planet explorer that will address the processes that shaped the rocky planets of the inner solar system (including Earth) more than four billion years ago
 - InSight will probe beneath the surface of Mars, detecting the fingerprints of the processes of terrestrial planet formation
- In January 2016, the March 2016 launch date of InSight mission was suspended to allow the repair of a leak in a section of the prime instrument in the science payload.



Battery Details

- Two 8-cell batteries (connected in parallel)
- Manufactured by Eagle-Picher Technologies / Yardney Division
- 24-32.8 V (Phoenix Battery Design)
- Qualification Temperature range: - 40°C to +50°C.
- **Operating Temperature Range: -30° to +35°C**
- **Required Life: ~ 4 years**
- **Surface Life: 709 Sols of operation.**

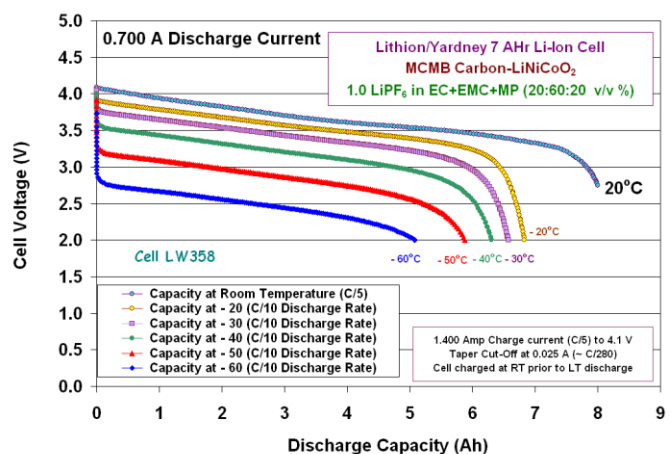
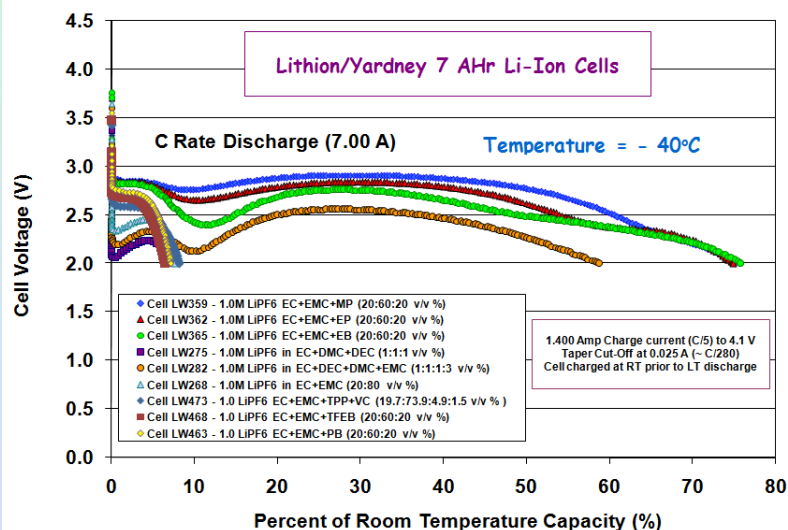
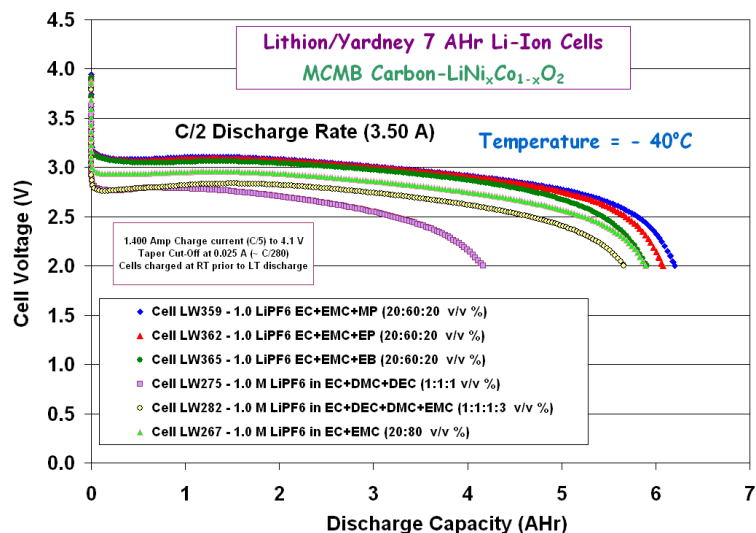


Development of Advanced Low Temperature Electrolytes

Demonstration of Ester-Based Electrolytes in Yardney Prototype Cells

Performance at -40°C (C/2 Rate)

Performance at -40°C (C Rate)



An electrolyte formulation containing methyl propionate, 1.0M LiPF₆ EC+EMC+MP (20:60:20 v/v %) was demonstrated to provide improved low temperature performance over baseline all carbonate-based electrolytes (including the heritage blend), while still providing reasonable high temperature resilience.

- M.C. Smart, and B.V. Ratnakumar, L.D. Whitcanack, K.A. Smith, S. Santee, R. Gitzendanner, V. Yevoli, "Li-Ion Electrolytes Containing Ester Co-Solvents for Wide Operating Temperature Range", *ECS Trans.* **11**, (29) 99 (2008).
- M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, "Lithium-Ion Electrolytes Containing Ester Co-solvents for Improved Low Temperature Performance", *J. Electrochem. Soc.*, **157** (12), A1361-A1374 (2010).



Performance Testing of Yardney NCP-25x Lithium-Ion Cells

Summary of Test Plan for InSight

➤ Next Generation Yardney NCP-25x Li-Ion Cells

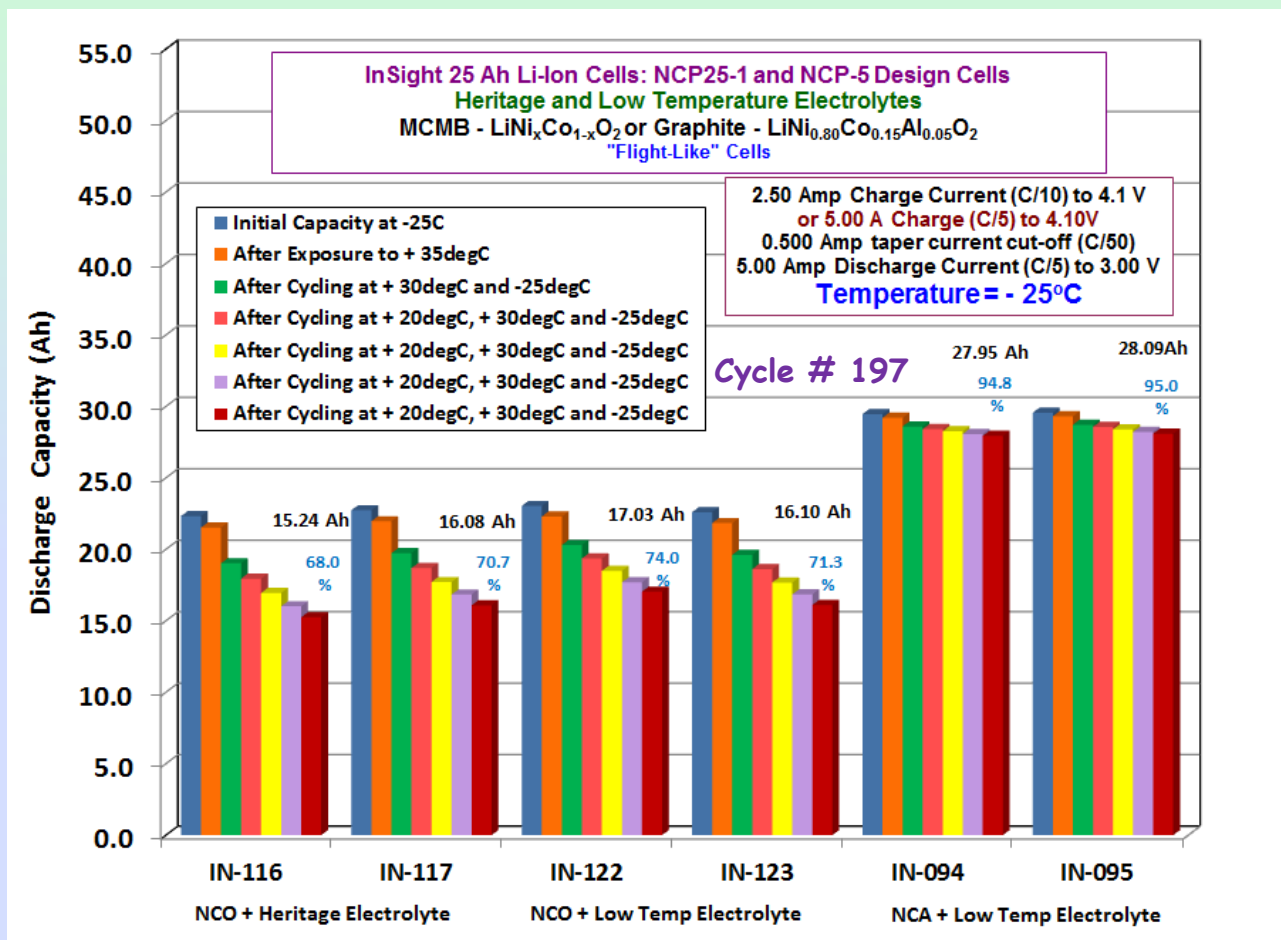
- 18 Cells were tested possessing four chemistry variations
- Cells are 25 Ah nameplate capacity (based on Yardney NCP-25-1 design)
- Cells were subjected to rigorous performance testing to determine applicability to InSight

Cell Group (Quantity)	Cell Definition	Cathode	Anode	Material Loading	Electrolyte
Chemistry A (5 Cells)	Heritage (Control / Phoenix Baseline)	LiNiCoO ₂ (NCO)	MCMB	Nominal	Standard Heritage Electrolyte 1.0M LiPF ₆ in EC+DEC+DMC (1:1:1)
Chemistry B (5 Cells)	Heritage, Low- Temperature Electrolyte	LiNiCoO ₂ (NCO)	MCMB	Nominal	Low-Ester, Low-Temperature 1.0M LiPF ₆ in EC+EMC+MP (20:60:20)
Chemistry C (5 Cells)	NextGen Chemistry, Low-Temperature Electrolyte	LiNiCoAlO ₂ (NCA)	Modified Graphite	Nominal	Low-Ester, Low-Temperature 1.0M LiPF₆ in EC+EMC+MP (20:60:20)
Chemistry D (3 Cells)	NextGen Chemistry, Heritage Electrolyte	LiNiCoAlO ₂ (NCA)	Modified Graphite	Nominal	Standard Heritage Electrolyte 1.0M LiPF ₆ in EC+DEC+DMC (1:1:1)



Performance Testing in Support of InSight

Summary of Results: Group 1 Cells (Discharge Capacity at -25°C)



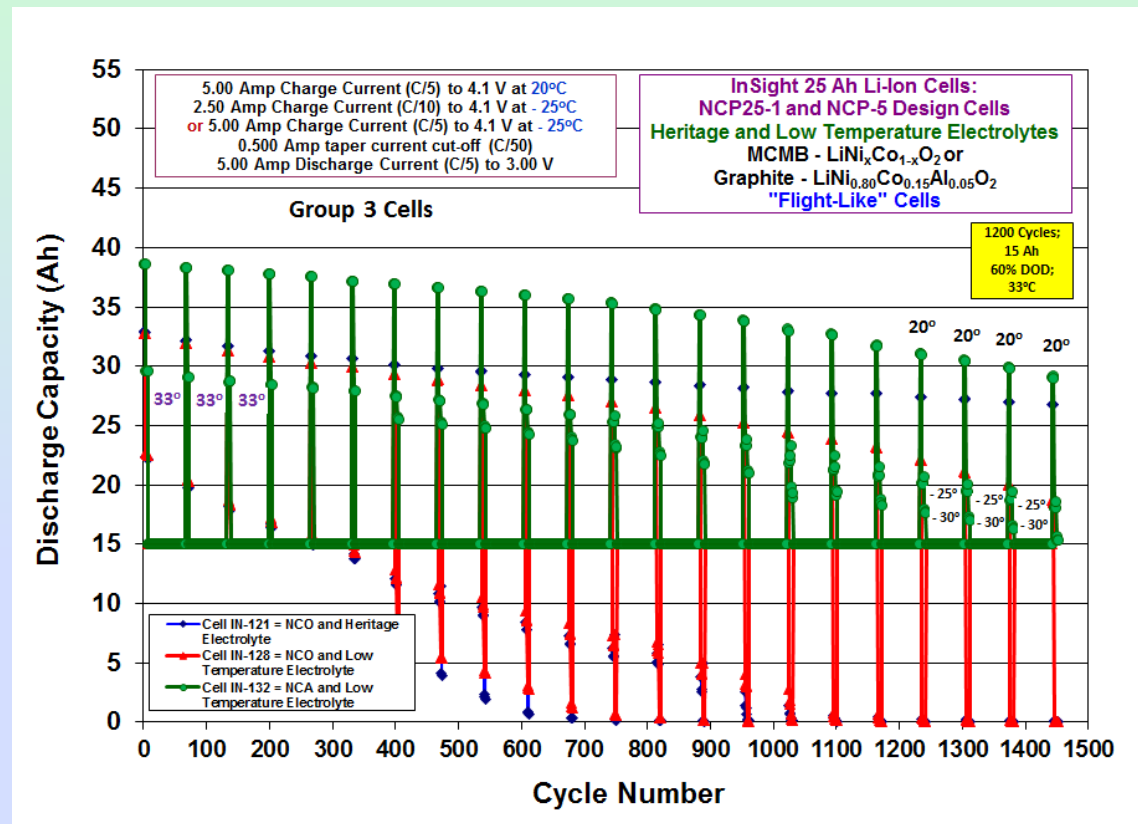
- The NCA+ Low Temperature Electrolyte chemistry delivers improved capacity at -25°C compared with the NCO heritage (> 78% improvement) and displays dramatically better low temperature capacity retention throughout the life of the cells.

M. C. Smart, S. F. Dawson, R. B. Shaw, L. D. Whitcanack, A. Buonanno, C. Deroy, and R. Gitzendanner, "Performance Validation of Yardney Low Temperature NCA-Based Li-ion Cells for the NASA Mars InSight Mission", NASA Aerospace Battery Workshop, Huntsville, Alabama, November 18-20, 2014.



Performance Testing in Support of InSight

Summary of Results: Group 3 (Discharge Capacity, Ah)



- The Group 3 cells were cycled at high temperature +33°C and periodically characterized at +20°, -25°, and -30°C
- The NCA+LTE cell IN-132 delivered 18.79 Ah at -25°C (cycle 1,378) and 16.31 Ah at -30°C (cycle 1,382)
In contrast, the NCO+Heritage only delivered 0.100 Ah and the NCO+LTE delivered 0.084 Ah at -25°C (cycle 1,378)
- Cells cycled under flight-like conditions (i.e., C/5 charge rate to 4.10V)
- Cells have completed 1,200 accelerated cycles at high temperature (i.e., 33°C)

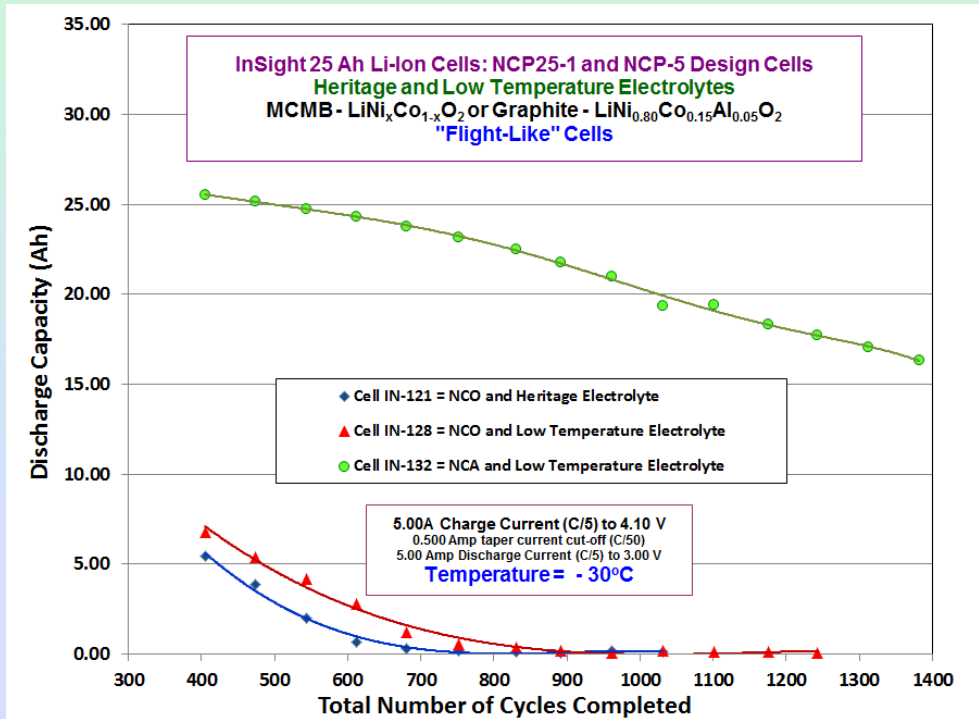
M. C. Smart, B. V. Ratnakumar, F. C. Krause, L. D. Whitcanack, E. A. Dewell, S. F. Dawson, R. B. Shaw, S. Santee, F. J. Puglia, A. Buonanno, C. Deroy, and R. Gitzendanner, "Performance Testing of Yardney Li-ion Cells in Support of NASA's MSL and InSight Missions", NASA Aerospace Battery Workshop, Huntsville, Alabama, November 17-19, 2015.

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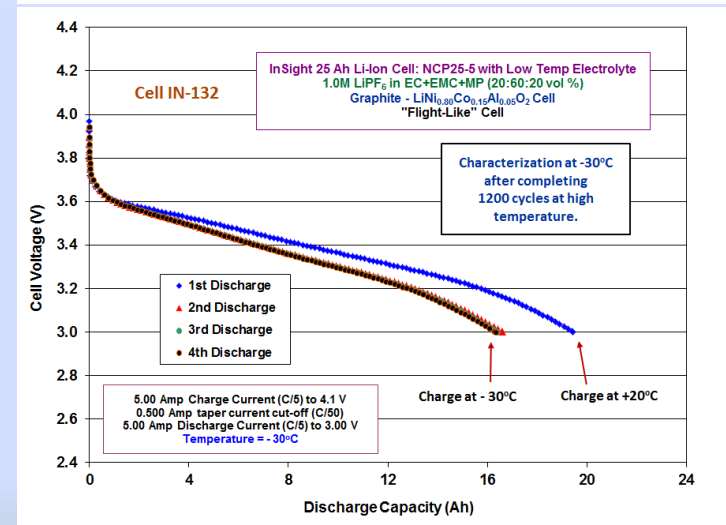
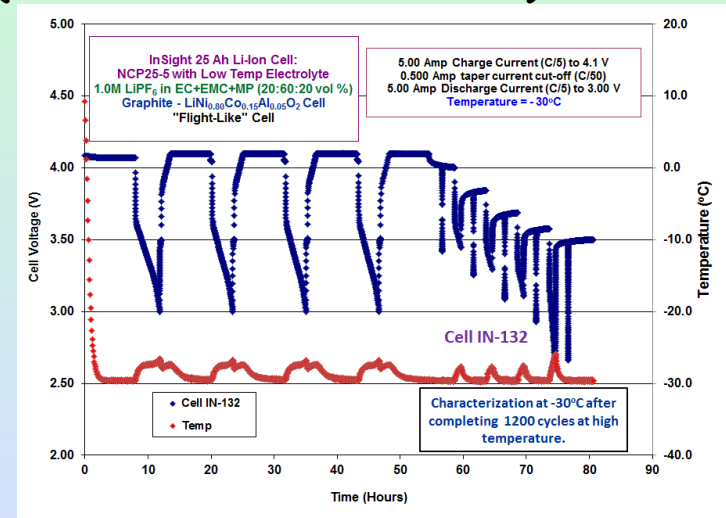


Performance Testing in Support of InSight

Summary of Results : Group 3 (Performance at -30°C)



- After completing 1080 high temperature cycles (and over 1240 total cycles), the NCA+LTE dramatically outperforms the heritage chemistry at -30°C (i.e., delivering 17.5 Ah compared with negligible capacity for the heritage cell)
- No evidence of Li plating was observed with the cells using a C/5 charge rate (5.0A) at -30°C.



M. C. Smart, B. V. Ratnakumar, F. C. Krause, L. D. Whitcanack, E. A. Dewell, S. F. Dawson, R. B. Shaw, S. Santee, F. J. Puglia, A. Buonanno, C. Deroy, and R. Gitzendanner, "Performance Testing of Yardney Li-ion Cells in Support of NASA's MSL and InSight Missions", NASA Aerospace Battery Workshop, Huntsville, Alabama, November 17-19, 2015.

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Background: Mission Concept Needs

Potential Future Ocean Worlds Power System Needs

- Power: ~ 100 W
- Voltage ~ 28 V
- Operational Life on Surface: 7-14 days
(2 - 4 Europa days)
- Mission Survivability/Shelf Life: 15 years
- Operating Temperature: - 60°C to 40°C
- Radiation Tolerance: > 2-4 Mrad
- Planetary Protection: Required
- A potential future mission to Europa, or other Ocean World, could benefit significantly from a low temperature rechargeable battery with full operational capability when coupled with solar arrays, enabling a means to meet a 14 day requirement:
 - If RHU's or RTG's were not selected to provide heat, low temperature batteries would be desired
 - Improved low temperature performance (**down to -60°C**) would reduce thermal power loads
 - Results in lower power sub-system and thermal power sub-system mass
 - Extended mission durations are possible (> 14 days)



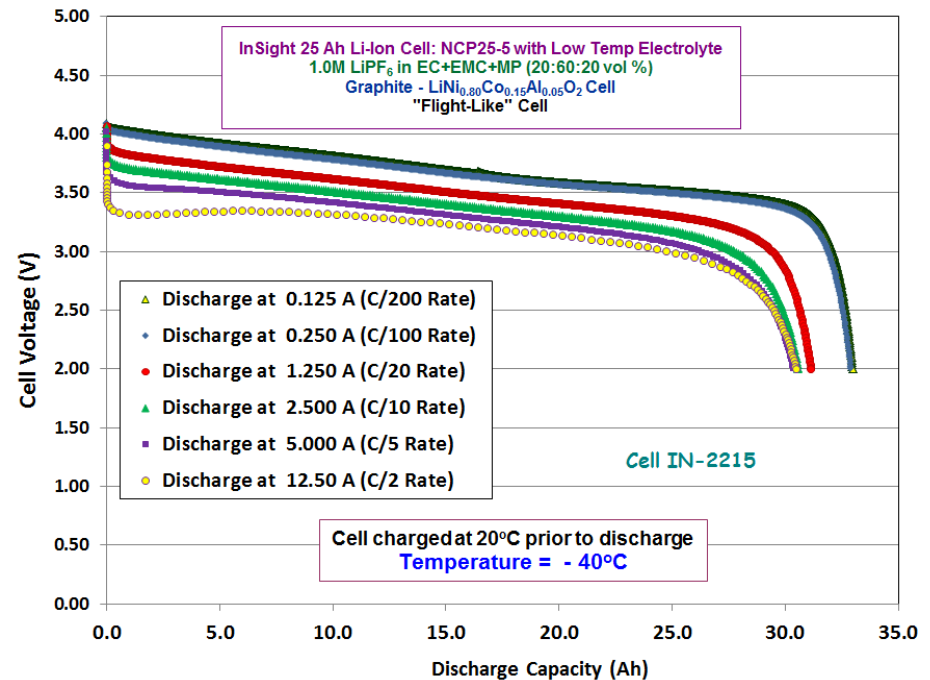
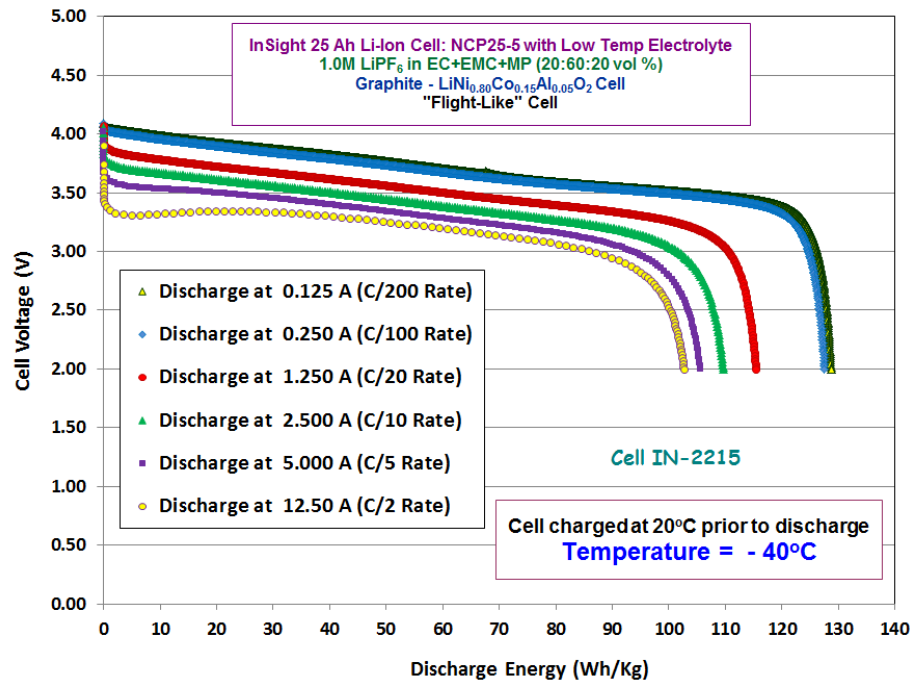
Pre-Decisional Information -- For Planning and Discussion Purposes Only

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Performance Testing of InSight Yardney NCP-25-6 Cells

Evaluation of Low Temperature Performance for Future Potential NASA Missions to Icy Moons



- The next generation InSight chemistry containing the MP-based low temperature electrolytes delivers good rate capability at -40°C , delivering over 102 Wh/kg at a C/2 rate (or 12.50A).
- Demonstrates that technology is well suited to support high power transmission events.

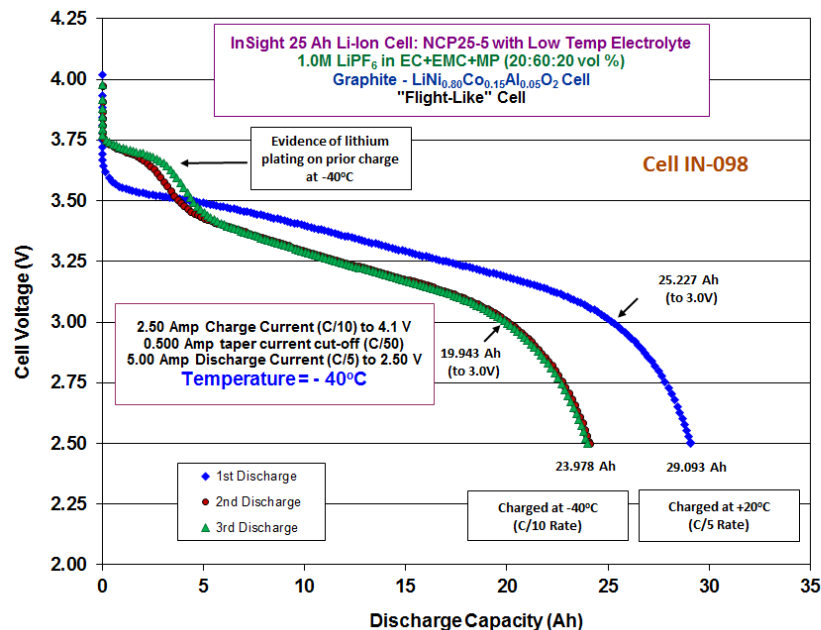
M. C. Smart. et al., "The Use of Low Temperature Electrolytes in High Specific Energy Li-Ion Cells for Future NASA Missions to Icy Moons", 229th Meeting of the Electrochemical Society, San Diego, California, June 1, 2016.



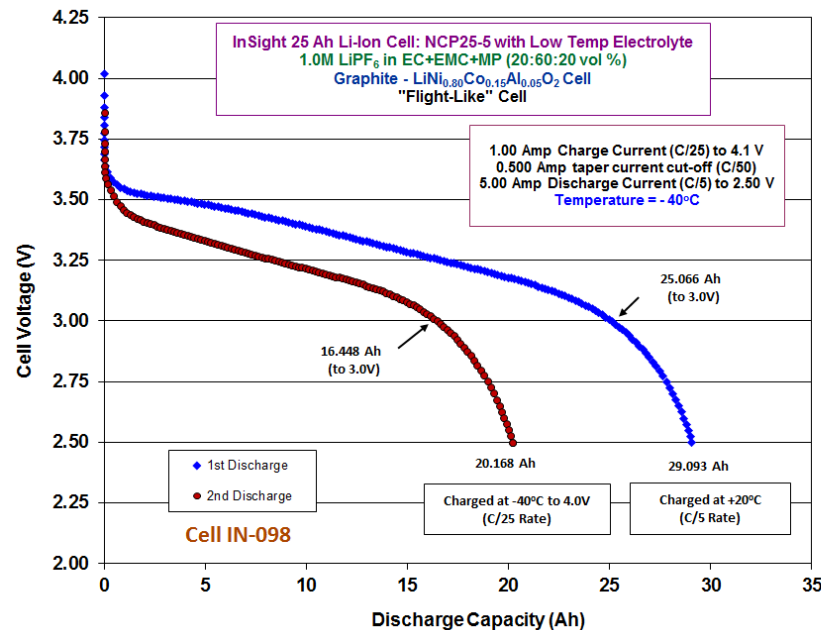
Performance Testing in Support of InSight Project

Charging and discharging at -40°C

C/10 (2.5A) to 4.10V at -40°C



C/25 (1.0A) to 4.00V at -40°C

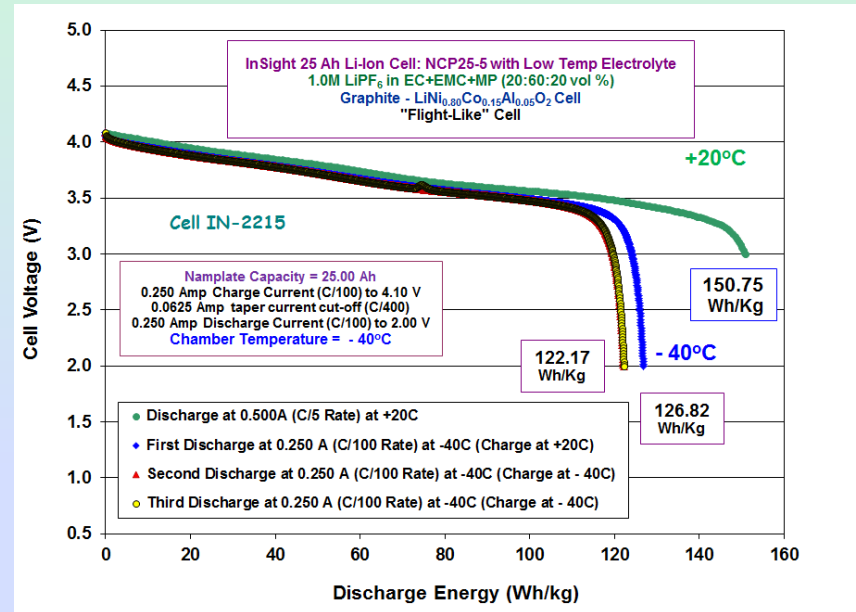
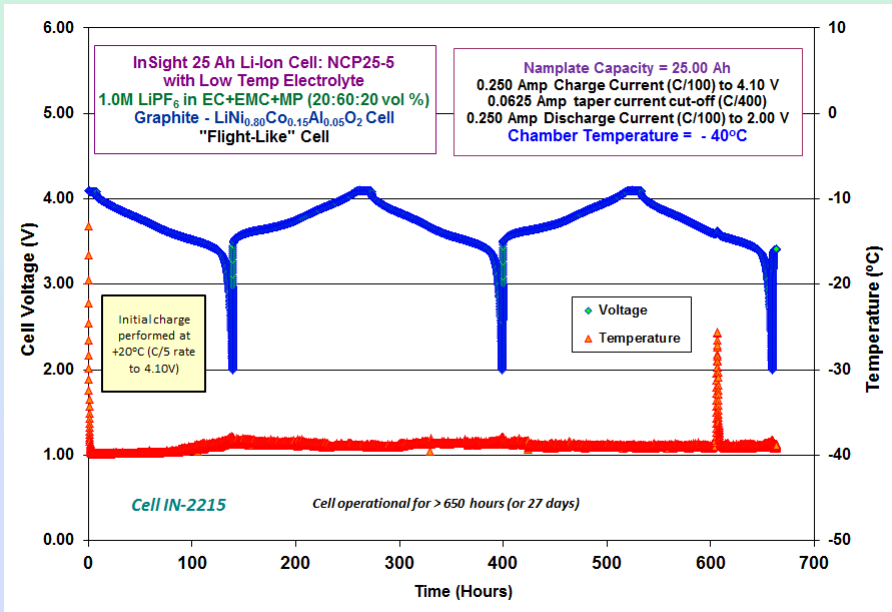


- When NCA/LTE cells were cycled at -40°C using C/10 charge rate, Li plating was observed on the anode
- This is indirectly observed by the higher voltage plateau on the subsequent discharge (i.e., the lower overpotential of lithium stripping compared to Li⁺ de-intercalation from graphite).
- Results led to the evaluation of lower charge rates and charge voltage test at -40°C (i.e., C/25 charge rate to 4.00V), where no evidence was observed.
- Subsequent testing established only modest plating at -35°C (C/5 rates to 4.10V) and no plating evident at -30°C (using C/5 charge rates to 4.10V)



Performance of InSight 36 Ah (Yardney NCP-25-1 Design) Li-Ion Cells: (Next Generation NCA Chemistry + Low Temperature Electrolyte)

Cycling Continuously at -40°C at C/100 Rates (both Charging and Discharging)



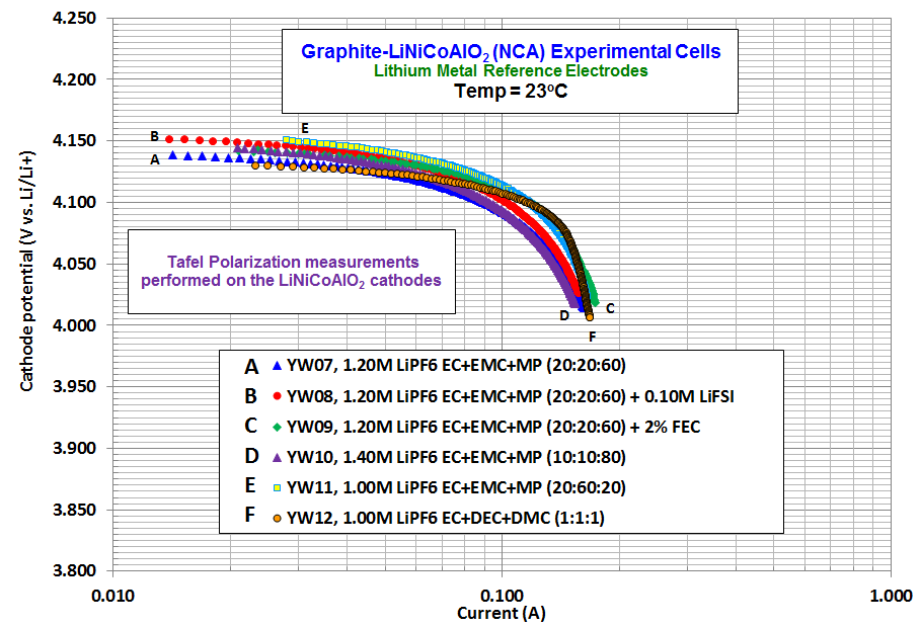
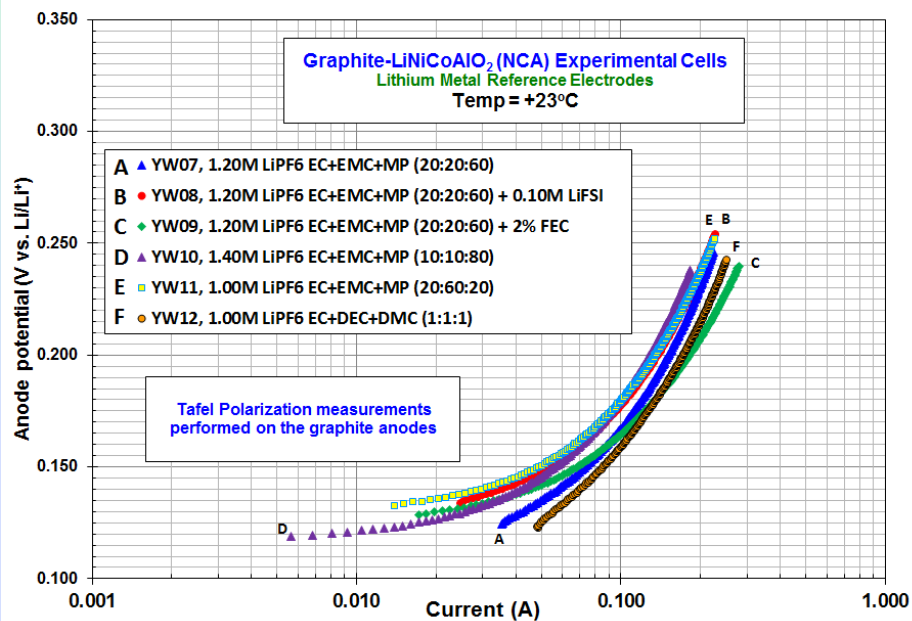
- The next generation InSight chemistry containing the MP-based low temperature electrolytes delivers good reversibility when cycled continuously at -40°C using low rates (i.e., delivering ~ 122 Wh/kg at -40°C).
- No evidence of lithium plating observed when cycled under these conditions.

➤ Performance demonstration exceeds target of 100 Wh/kg at -40°C .



Performance of Eagle-Picher/Yardney Experimental 3-Electrode Cells (Electrodes obtained from Yardney)

Tafel Polarization Measurements at +23°C

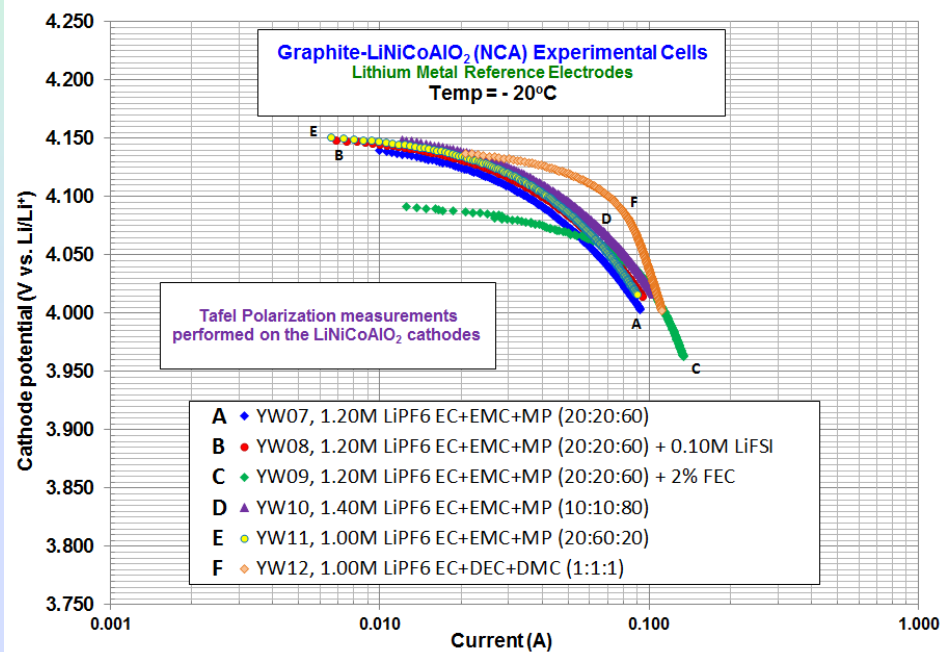
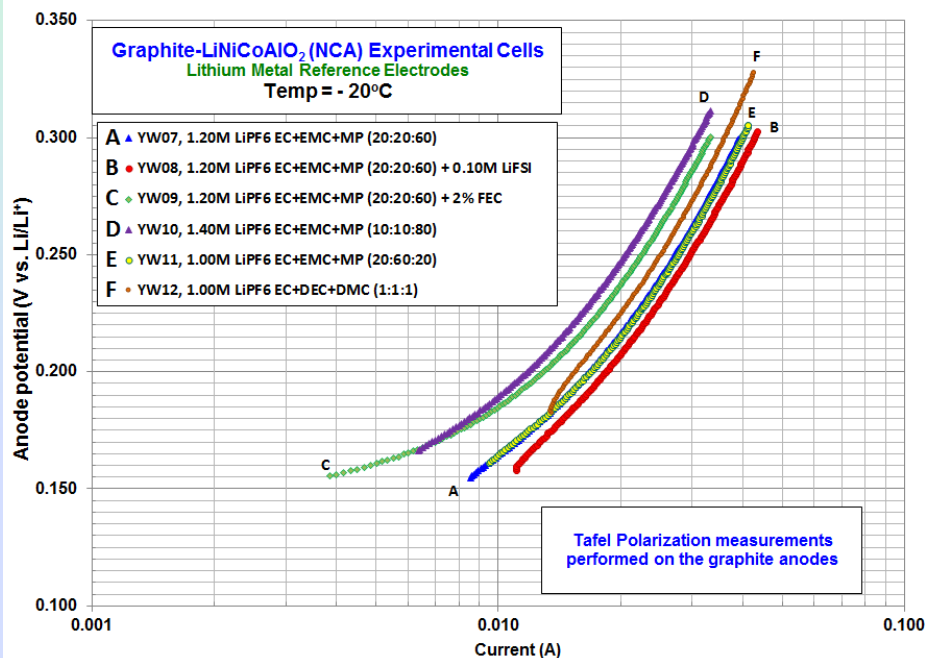


- When Tafel polarization measurements are performed at 23°C, the kinetics of the NCA cathodes and graphite anode are relatively comparable, with the cathodes displaying modestly impeded kinetics.
- Both ester-based electrolytes and the all carbonate based electrode display similar characteristic.
- The use of FEC as an electrolyte additive was observed to improve the lithium kinetics at both the anode and cathode.



Performance of Eagle-Picher/Yardney Experimental 3-Electrode Cells (Electrodes obtained from Yardney)

Tafel Polarization Measurements at - 20°C

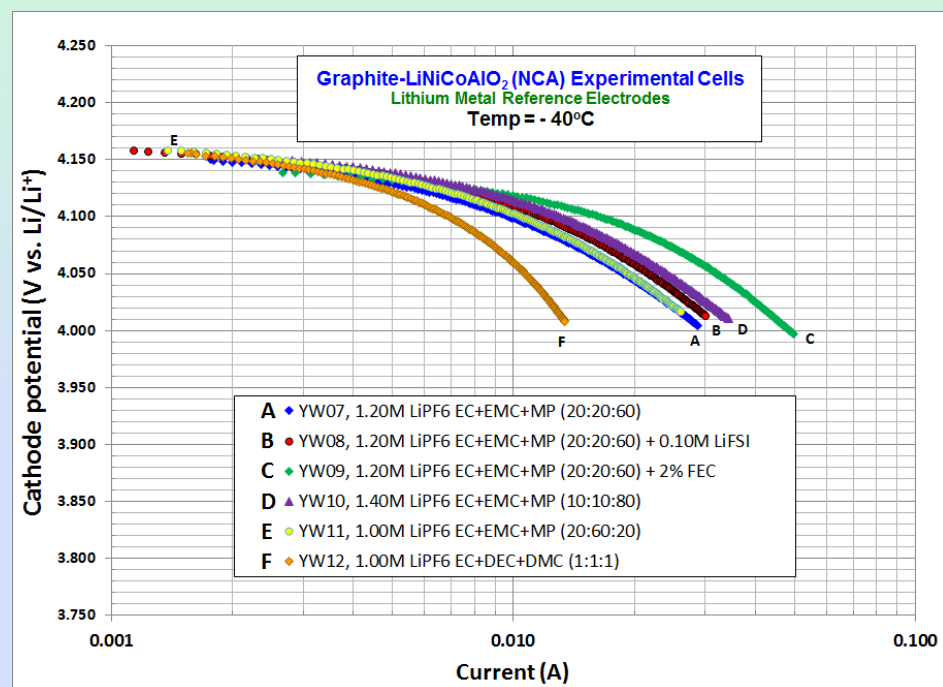
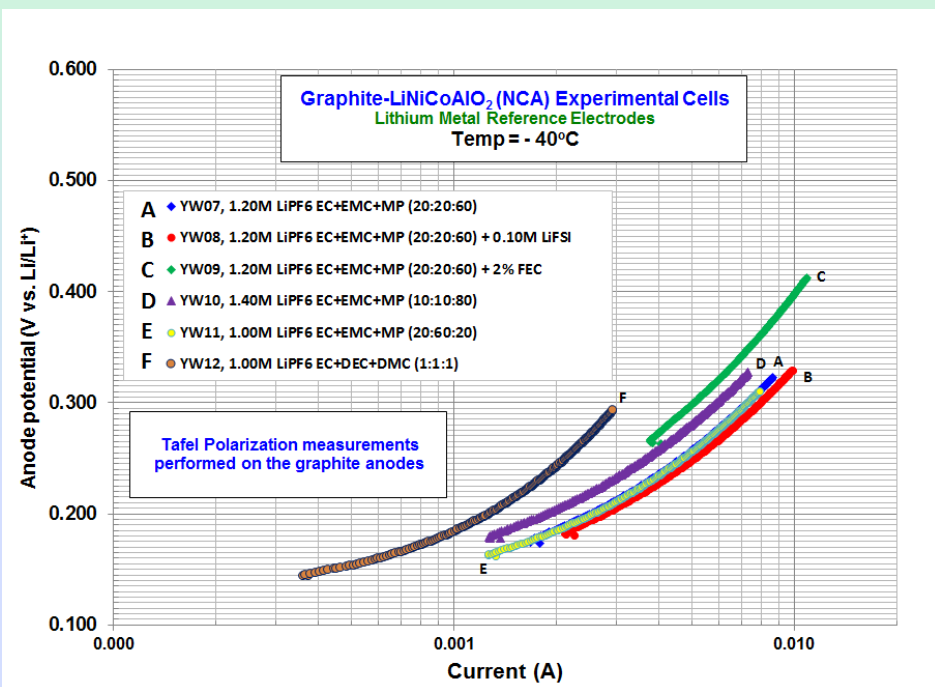


- When Tafel polarization measurements are performed at -20°C, the kinetics of the NCA cathodes are superior to that of the graphite anodes.
- The conditions of increased polarization resistance at the anode compared to the cathode is generally not desirable, due to the increased propensity of lithium plating to occur.



Performance of Eagle-Picher/Yardney Experimental 3-Electrode Cells (Electrodes obtained from Yardney)

Tafel Polarization Measurements at -40°C

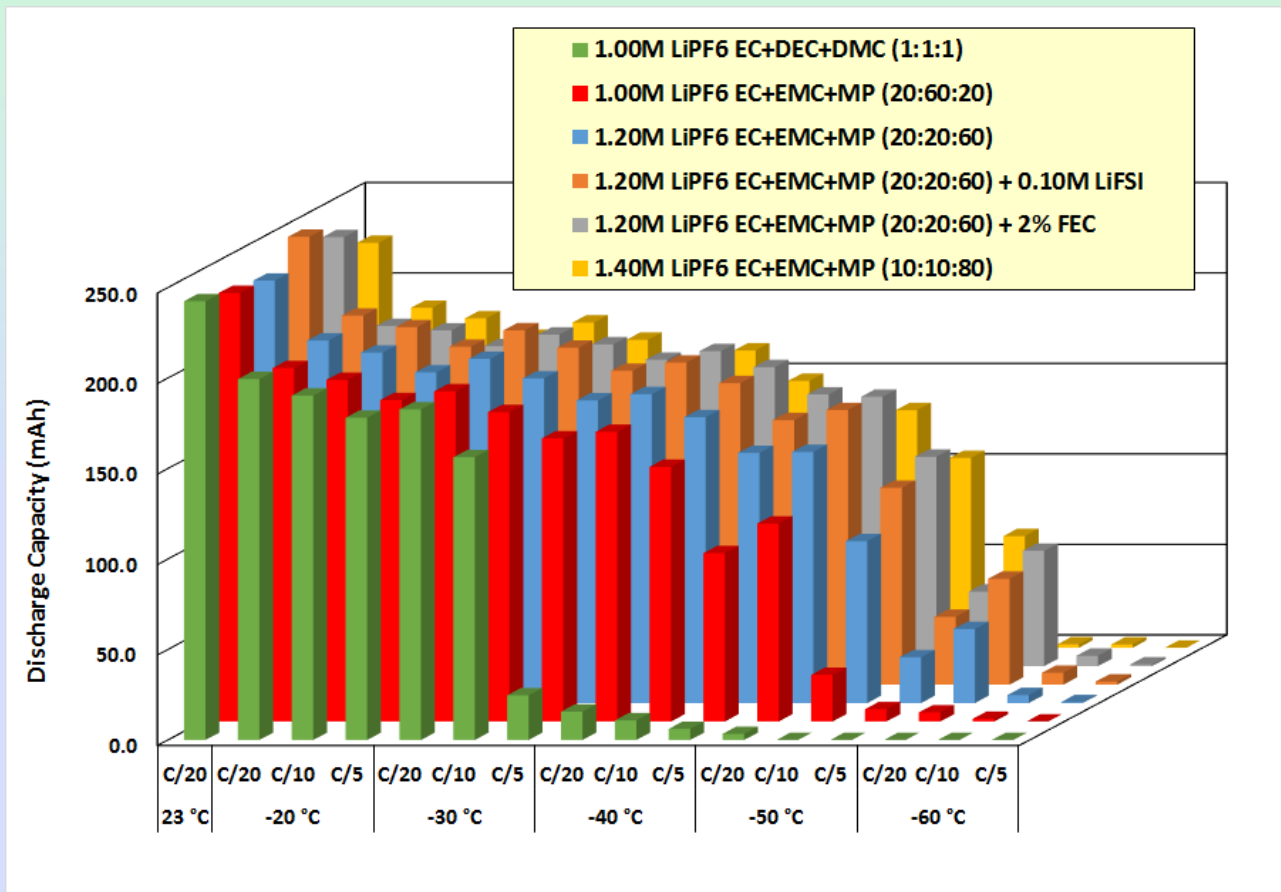


- When Tafel polarization measurements are performed at -40°C, the kinetics of the NCA cathodes are much more facile than the graphite anodes.
- The methyl propionate (MP)-based electrolytes display improved lithium kinetics at both the anode and cathode compared with the all carbonate-based baseline electrolyte.
- The addition of both FEC and LiFSI lead to improved lithium de-intercalation kinetics at the anode.



Performance of Eagle-Picher/Yardney Experimental 3-Electrode Cells (Electrodes obtained from Yardney)

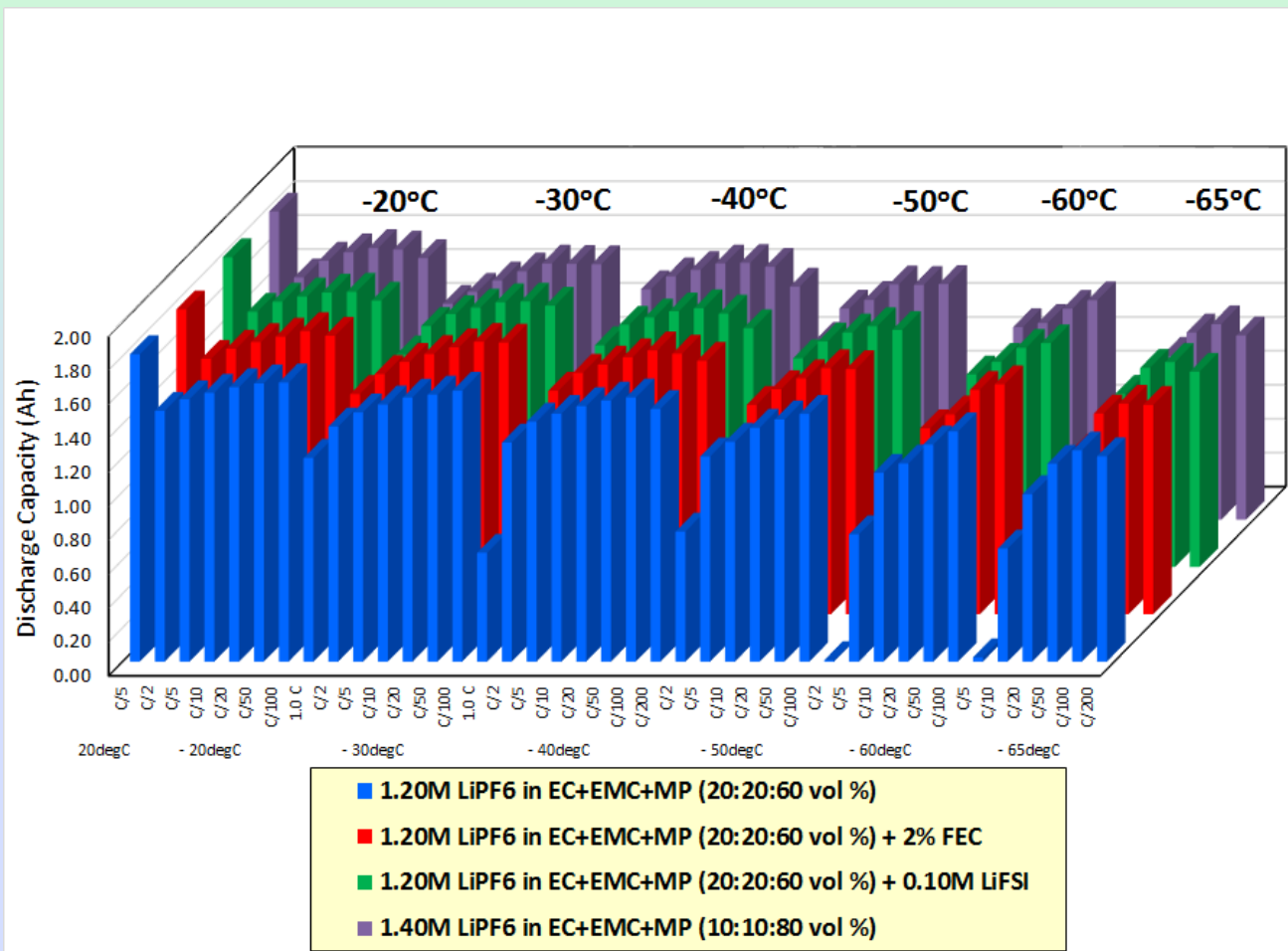
Low Temperature Discharge Characterization (-20°C to -60°C)



- The electrolytes with a large proportion of methyl propionate displayed the best low temperatures performance.
- The addition of both FEC and LiFSI lead to improved capability at high rates at very low temperatures.



Performance of Eagle-Picher/Yardney Experimental 1.80 Ah Pouch Cells Low Temperature Discharge Characterization (-20°C to -65°C)

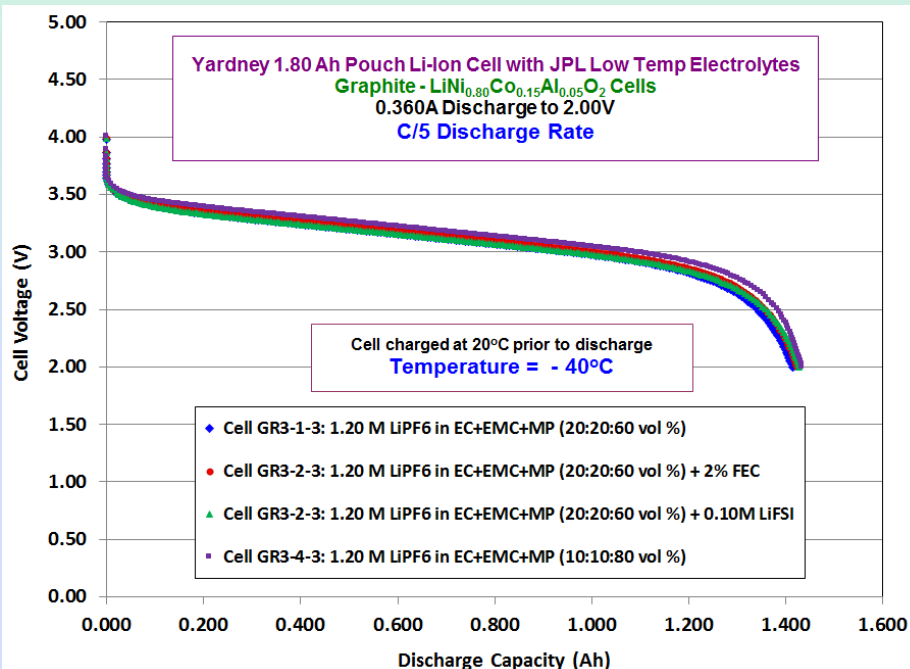


- All of the methyl propionate-based electrolyte evaluated in 1.80Ah prototype pouch cells displayed comparable low temperatures performance, performing well down to -65°C.
- The use of FEC and high MP content lead to modestly improved capability at high rates at very low temperatures.

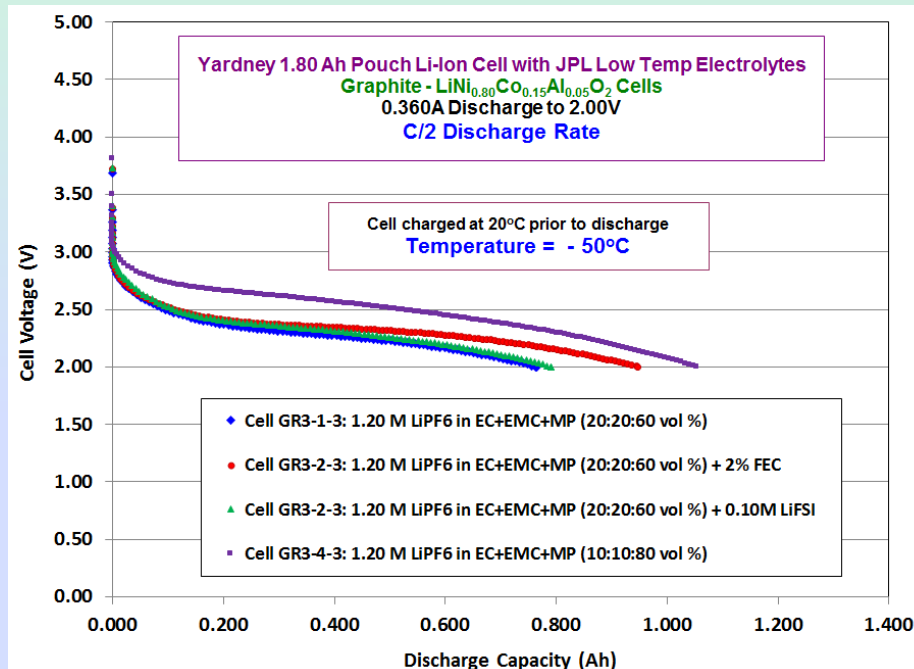


Performance of Eagle-Picher/Yardney Experimental 1.80 Ah Pouch Cells Low Temperature Discharge Characterization (-20°C to -65°C)

C/5 Discharge at -40°C



C/2 Discharge at -50°C

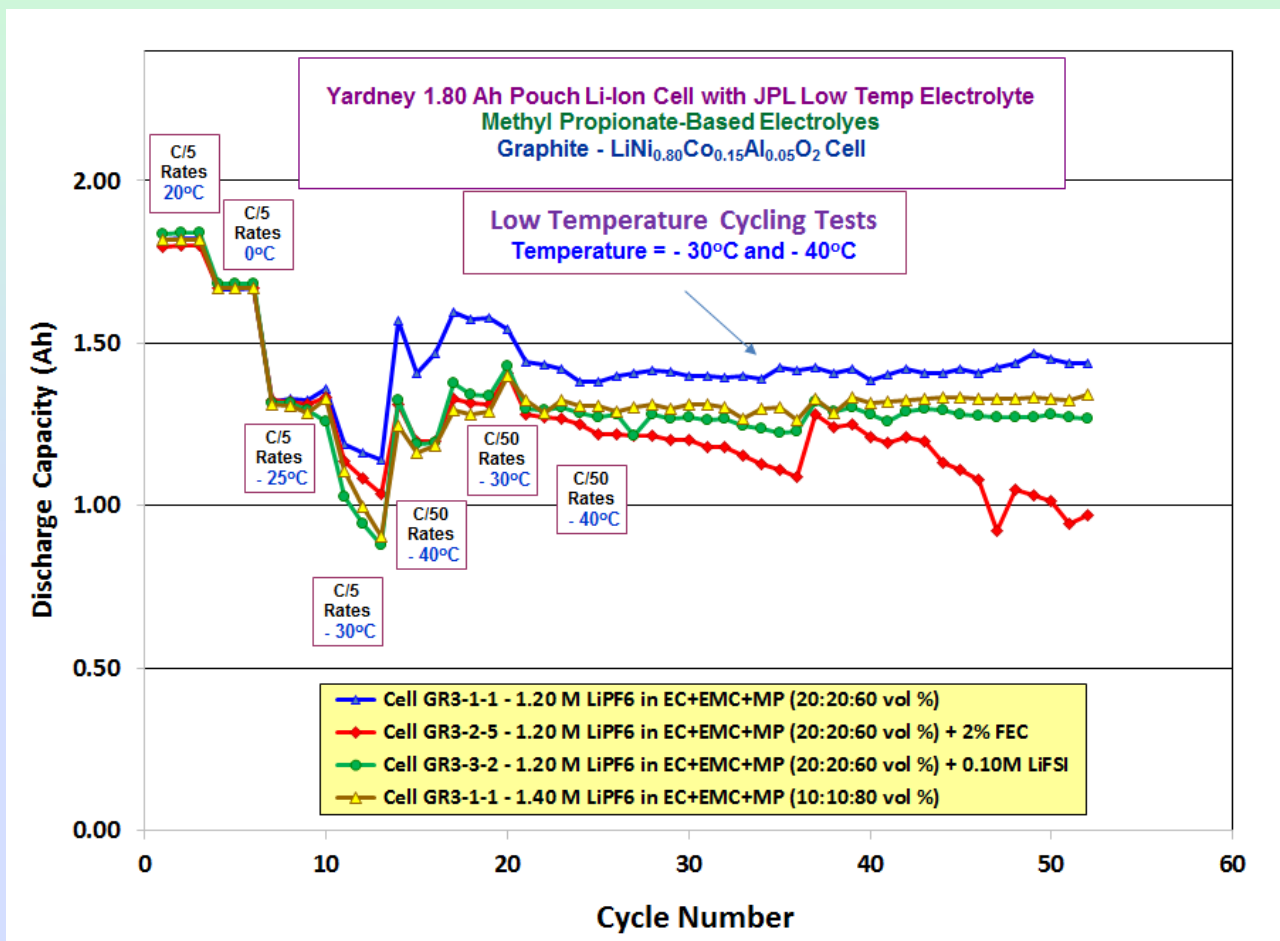


- All of the methyl propionate-based electrolyte evaluated in 1.80Ah prototype pouch cells displayed comparable low temperatures performance, performing well down to -65°C.
- The use of FEC and high MP content lead to modestly improved capability at high rates at very low temperatures.



Performance of Eagle-Picher/Yardney Experimental 1.80 Ah Pouch Cells

Cycle Life Performance at -30°C and -40°C



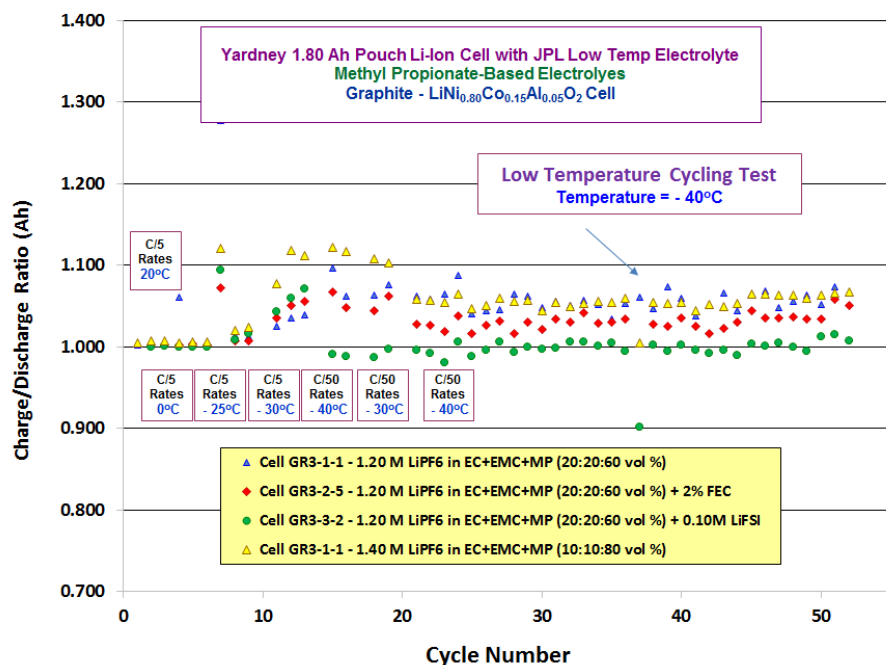
- The cells containing the methyl propionate-based electrolyte containing no additives displayed the highest capacity when continuously cycled at -40°C.
- The cell containing FEC displayed the highest capacity, suggesting continued build-up of SEI and/or CEI films..



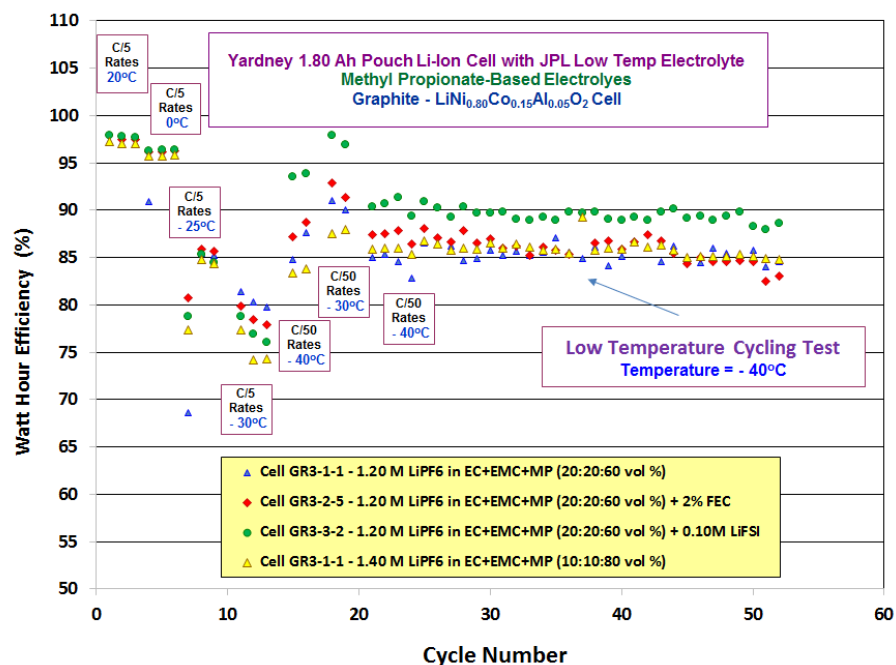
Performance of Eagle-Picher/Yardney Experimental 1.80 Ah Pouch Cells

Cycle Life Performance at -30°C and -40°C

Charge/Discharge Ratio (Ah)



Watt Hour Efficiency (%)



- When continuously cycled at -40°C, the cell containing the LiFSI additive displayed the lowest charge/discharge ration and the highest watt-hour efficiency, suggesting that it contribute to efficient charge characteristics.
- These trends are expected to be more dramatic with the use of higher charge rates at low temperature.



➤ ***Summary and Conclusions:***

- The SOP heritage all carbonate chemistry has been demonstrated to display good low temperature performance and life over a temperature range of -20°C to +40°C.
 - Electrolyte used on MER, Phoenix, Juno, Grail, and MER
- Due to the need for good low temperature capability throughout the mission, and the favorable results obtained with this testing program, the InSight project has adopted the NCA+LTE chemistry for the flight battery. This involves using a methyl propionate containing electrolyte.
- Beginning of life (BOL), the NCA-based cells delivered >15% improvement in the capacity and energy delivered at ambient temperature and 31% more capacity at -25°C compared to the NCO-based chemistries.
- The SOA aerospace Li-ion InSight chemistry containing a JPL developed MP-based low temperature electrolytes delivers good reversibility when cycled continuously at -40°C using low rates (i.e., delivering ~ 122 Wh/kg at -40°C).
- Electrolytes with high proportions of methyl propionate have been demonstrated to have improved low temperature performance in experimental three electrode cells and 1.80Ah pouch cells.
 - The methyl propionate (MP)-based electrolytes display improved lithium kinetics at both the anode and cathode at low temperature compared with the all carbonate-based baseline electrolyte.
 - The use of FEC and high MP content lead to modestly improved capability at high rates at very low temperatures.
 - When cycled at -40°C, the cell containing the LiFSI additive displayed the lowest charge/discharge ration and the highest watt-hour efficiency, suggesting that it contribute to efficient charge characteristics.



Acknowledgments

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